TERTIARY ALCOHOL DERIVATIVES OF 2-ACETYLTHIOPHENE

A THESIS

Presented to

the Faculty of the Division of Graduate Studies

Georgia Institute of Technology

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemistry

by

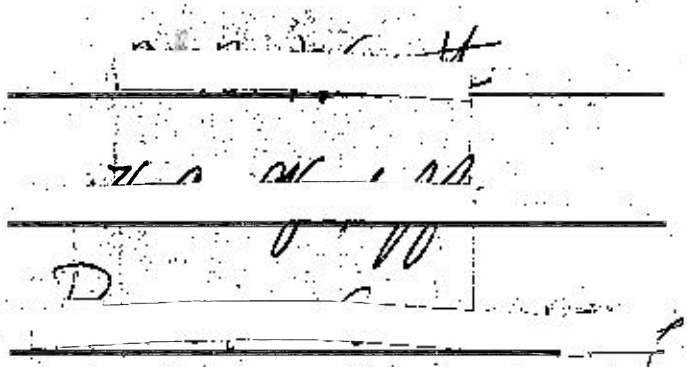
Raymond Peter Nejak

September 1951

TERTIARY ALCOHOL DERIVATIVES

OF 2-ACETYLTHIOPHENE

Approved:



Date Approved by Chairman: February 29, 1952

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation for the valuable counsel generously offered by Dr. E. Emmett Reid and Professor B. B. Wroth.

TABLE OF CONTENTS

CHAPTER I

HISTORICAL REVIEW

TERTIARY ALCOHOL DERIVATIVES

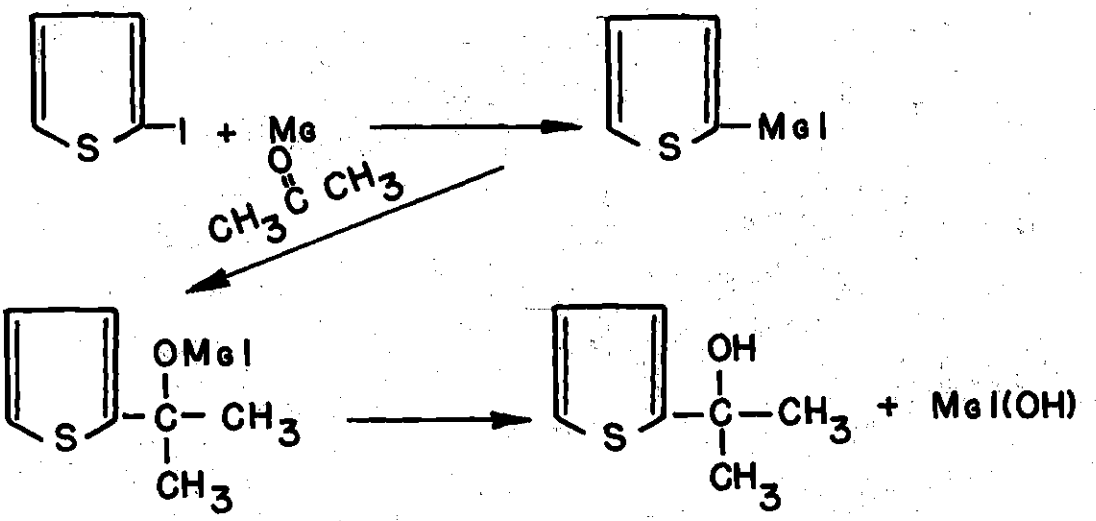
OF 2-ACETYLTHIOPHENE

CHAPTER I

HISTORICAL REVIEW

By the condensation of 2-acetylthiophene with a sequence of normal alkylmagnesium halides, a homologous series of disubstituted tertiary alcohols can be prepared through the Grignard reaction. The general formula for such a series is of the nature $C_nH_{2n-4}SO$. The factor of increment in this series is CH_2.

The lowest possible thienylcarbinol of the series $C_nH_{2n-4}SO$, dimethyl 2-thienylcarbinol, was first prepared by Thomas[1] through the condensation of 2-thienylmagnesium iodide and acetone.



[1]Thomas, V., Compte rendus 146, 643

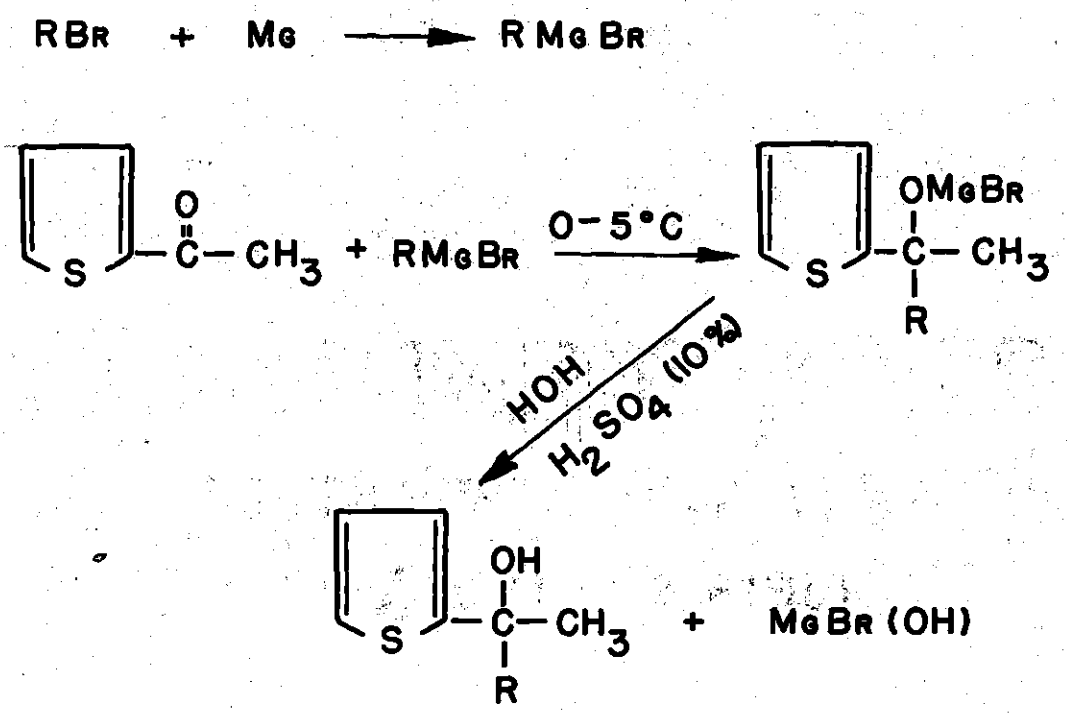
Thomas, however, was unsuccessful in attempts to prepare methylethyl 2-thienylcarbinol and methyl n-amyl 2-thienylcarbinol by the reaction of methyl ethyl ketone and methyl n-amyl ketone, respectively with 2-thienylmagnesium iodide. A highly competitive dehydration reaction apparently rendered the isolation of the carbinols exceedingly difficult.

William M. Beaver[2] by employing a condensation technique involving 2-acetylthiophene and appropriate alkylmagnesium iodides, was successful in isolating dimethyl 2-thienylcarbinol, methylethyl 2-thienylcarbinol, methyl n-propyl 2-thienylcarbinol, methylisopropyl 2 thienylcarbinol, methyl n-butyl 2-thienylcarbinol, methylisobutyl 2-thienylcarbinol, methyltertiary butyl 2-thienylcarbinol, methyl n-amyl 2-thienylcarbinol, and methyl n-hexyl 2-thienylcarbinol. The alcohols were described as colorless to light yellow oils possessing a characteristic pungent odor. Beaver determined the yield, boiling point, density (20°C), refractive index (20°C), molecular refraction, and the carbon and hydrogen content of each carbinol.

---

[2]Beaver, William M., Tertiary Alcohol Derivatives of 2-Acetylthiophene," Thesis, School of Chemistry, Georgia Institute of Technology, 1950

The method of synthesis utilized by Beaver may be pictured in this fashion.



CHAPTER II

PURPOSE OF THIS INVESTIGATION

CHAPTER II

PURPOSE OF THIS INVESTIGATION

The purpose of this investigation is to extend the series $C_nH_{2n-4}SO$ of tertiary alcohols by the preparation, isolation, and the determination of the properties of methyl n-heptyl 2-thienylcarbinol, methyl n-octyl 2-thienylcarbinol, methyl n-nonyl 2-thienylcarbinol, methyl n-decyl 2-thienylcarbinol, methyl n-undecyl 2-thienylcarbinol, and methyl n-dodecyl 2-thienylcarbinol.

Large quantities of thiophene are now becoming available commercially. Each contribution to the development of new thiophene derivatives increases understanding in this comparatively unexplored synthetic field, and makes more material the possibility of practical application for thiophene and thiophene derivatives.

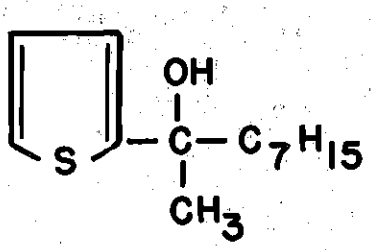
CHAPTER III

EXPERIMENTAL

CHAPTER III

EXPERIMENTAL

The Preparation of Methyl n-Heptyl 2-Thienylcarbinol



Fourteen grams (0.562 moles) of magnesium turnings and 50 ml. of absolute ether were added to a 500 ml. three neck flask fitted with a dropping funnel, a condenser, and a power driven mercury seal stirrer. The system, strongly heated previous to the addition of reactants in order to drive out traces of moisture, was reheated to the point of moderate ether reflux. It was assumed that the development of an ether atmosphere would assist materially in minimizing the possibility of oxidation of the Grignard reagent. Subsequently, with constant stirring, 98.4 gm. (0.55 moles) of n-heptyl bromide dissolved in 75 ml. of absolute ether were added at a constant rate to the magnesium in the reaction flask over a period of 45 minutes. The addition of the bromide was regulated so as to allow the exothermic nature of the reaction to support a constant reflux of ether. The Grignard solution thus prepared was almost black in color.

Upon complete addition of the n-heptyl bromide, the reaction mixture was stirred for an additional twenty minutes. The Grignard

solution was then cooled in an ice water bath for 25 minutes, and 35.6 gm. (0.282 moles) of 2-acetylthiophene (redistilled at 101°-103°C and 8-10 mm.) dissolved in 50 ml. of absolute ether were added at a constant rate over a period of sixty minutes. Here again reaction was strongly exothermic in nature, and ice water cooling was necessary to maintain a reaction temperature range of 0-10°C. During the addition of the 2-acetylthiopene, the formation of a yellow colored precipitate was observed. Stirring was continued for 30 minutes after complete addition of the 2-acetylthiopene.

In order to induce hydrolysis, the Grignard complex was slowly added with vigorous stirring to 200 ml. of 25% ammonium chloride solution mixed with approximately 200 grams of ice. The product of hydrolysis was filtered. About 0.75 gm. of unreacted magnesium were recovered. The filtrate was extracted with three 200 ml. portions of ether, and the yellow colored extract was washed twice with water to remove traces of ammonium chloride and placed over anhydrous potassium carbonate for 24 hours.

The potassium carbonate was filtered out of the extract, and the residue was distilled over a water bath maintained at 45-50°C. This sufficed to remove most of the ether. The residue of this distillation was transferred to a 250 ml. Claisen flask fitted with a thermometer and an ebullition stick, and vacuum distilled over an oil bath at a rapid rate. A 25 ml. fraction of a clear, faintly yellow oil was isolated in the range 157°-159°C at 6-7 mm.

Qualitative observation of an infrared spectrophotometric analysis gave strong evidence of the presence of the OH functional grouping. A well defined adsorption band was observed at approximately 2.88 microns.

Combustion analysis of the product which boiled at 146°-147°C and 12 mm. gave the results 68.44% C and 9.79% H as compared to the calculated values of 68.96% C and 9.80% H for methyl n-heptyl 2-thienylcarbinol.

The molecular refraction of the product as calculated by the Lorentz-Lorentz equation was 67.64 as compared to the theoretical value of 68.64 for methyl n-heptyl 2-thienylcarbinol.

The product was obtained in a yield of 54.29%, and the refractive index and the density were found to be 1.5035 and 0.9897, respectively.

In an attempt previous to the successful preparation of methyl n-heptyl 2-thienylcarbinol a product was isolated which gave a molecular refraction value and a combustion value which corresponded quite closely to that expected for the dehydration product of the carbinol.

Experimental combustion results of 74.66% C and 9.76% H were obtained; the calculated carbon and hydrogen content of the olefin, 2-(2-thienyl) nonene-2, is 74.81% and 9.69% H.

The molecular refraction of the product was found to be 65.68 as compared to the theoretical olefin molecular refraction value of 66.65.

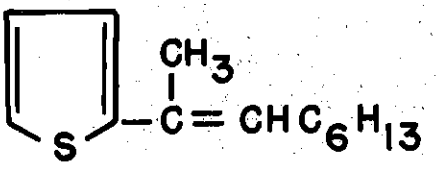
At 20°C the density and the refractive index of the product were determined to be 0.9623 and 1.5222, respectively.

The 2-(2-thienyl) nonene-2 was a yellow pungent oil which boiled at 142°C and 10 mm. It was obtained in a yield which was 33.61% of the theoretical yield.

In the process of dehydration of methyl n-heptyl 2-thienylcarbinol two routes are open with respect to the direction of dehydration. Primarily bonded hydrogen atoms are available adjacent to the hydroxylated carbon, and secondarily bonded hydrogen atoms are also available adjacent

to the hydroxylated carbon atom. In dehydration of alcohols, however, hydrogen is eliminated preferentially from the adjacent carbon atom that is poorer in hydrogen.[3]

Therefore we might expect a formula of such a nature for the olefin, 2-(2-thienyl) nonene-2:



In the preparation of the olefin 14 gm. of Mg turnings (0.583 moles) and 100 ml. of absolute ether were added to the dry reaction flask of an apparatus setup similar to that utilized in the synthesis of methyl n-heptyl 2-thienylcarbinol. Over a period of thirty minutes 107.3 gm. (0.599 moles) of n-heptyl bromide dissolved in 75 ml. of absolute ether were added to the reaction flask at a regular rate. After complete addition of the bromide, the reaction flask was cooled to 0°-5°C, and 69.3 gm. (0.55 moles) of 2-acetylthiophene dissolved in 50 ml. of ether were added. Stirring was continued for thirty minutes after complete addition of the 2-acetylthiophene.

The reaction mixture was then hydrolyzed by pouring the Grignard complex into a 10% H_2SO_4 solution mixed with 400 gm. of ice. Filtration

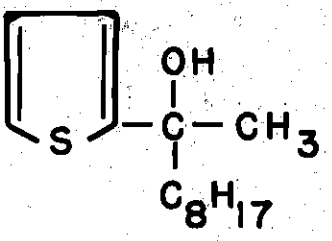
---

[3]Fieser, L. F., and Fieser, M., Organic Chemistry 1944, D. Heath and Company, p. 129.

removed traces of magnesium turnings. The filtrate was extracted three times with 200 ml. portions of ether.

The yellow extract was distilled so as to remove the ether, and the residue was transferred to a 250 ml. Claisen flask fitted with an ebullition tube and a thermometer, vacuum distillation was effected over a heating mantle.

The Preparation of Methyl n-Octyl 2-Thienylcarbinol



Fourteen grams of magnesium turnings (0.583 moles) and 50 ml. of absolute ether were added to the reaction flask of an apparatus setup exactly similar to that utilized in the preparation of methyl n-heptyl 2-thienylcarbinol, and heat sufficient to induce ether reflux was applied. Then 109.23 gm. of n-octyl bromide (0.566 moles) dissolved in 75 ml. of absolute ether were added to the Mg in the reaction flask. The addition required 30 minutes. The reaction mixture was cooled to 0-10°C, and over a period of 90 minutes 30.6 ml. (0.282 moles) of 2-acetylthiophene dissolved in 50 ml. of absolute ether were added. The formation of a light yellow precipitate was observed. The reaction mixture was stirred for thirty minutes after complete addition of the 2-acetylthiophene.

Hydrolysis was effected by slowly pouring the reaction products into a mixture of 200 ml. of 25% ammonium chloride solution and 200 gm. of ice. The hydrolyzed material was filtered and a small quantity of magnesium turnings was isolated. The filtrate was extracted with ether, and the ether extract, after washings with water, was placed over anhydrous potassium carbonate for a period of 24 hours. The residue of a subsequent

ether distillation was vacuum distilled at a rapid rate. Eighteen ml. of a light yellow oil were isolated at 168°C and 10 mm. pressure.

An infrared analysis of this fraction gave strong indication of the presence of the OH factor by a strong adsorption band at 2.88 microns.

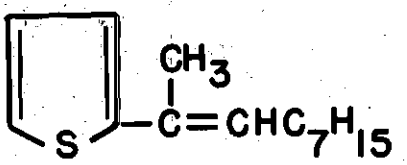
Combustion analysis of the product gave values of 70.63% C and 10.16% H. The calculated carbon and hydrogen content of methyl n-octyl 2-thienylcarbinol is 69.92% C and 10.07% H.

The molecular refraction of the product was determined to be 72.00 as compared to a theoretical value of 73.26.

The refractive index of the product was determined to be 1.5023, and the density was found to be 0.9669.

The carbinol was obtained in a yield of 37.06% and had a boiling point of 161°C at 14 mm. pressure.

An initial attempt at the production of methyl n-octyl 2-thienyl-carbinol led to the isolation of 2-(2-thienyl) decene-2.



Fourteen grams of magnesium turnings, a crystal of iodine, and 100 ml. of absolute ether were admitted to the reaction flask of an apparatus setup similar to that used in previous experiments.

One hundred and twelve gm. of n-octyl bromide (0.580 moles) dissolved in 75 ml. of absolute ether were slowly dropped into the reaction

flask over a period of 40 minutes. Stirring was continued for thirty minutes after the complete addition of the halide. The resulting Grignard solution was black in color. Much free magnesium was observed in the reaction flask. Sufficient heat to induce ether reflux was applied to further the reaction.

The solution was cooled, and 69.3 gm. of 2-acetylthiophene (0.55 moles) dissolved in 75 ml. of absolute ether were added over a period of 30 minutes. Stirring was continued for 45 minutes after addition of all the 2-acetylthiophene.

The reaction mixture was then hydrolyzed with 15% sulfuric acid and filtered. Approximately two grams of unreacted magnesium residue were isolated. The filtrate was extracted twice with ether, and the extract was stored over anhydrous K_2CO_3 for 48 hours.

After filtering out the potassium carbonate, the ether of the extract was distilled off, and the residue was placed into a 250 ml. Claisen flask fitted with an ebullition tube and a thermometer. Distillation under vacuum was effected.

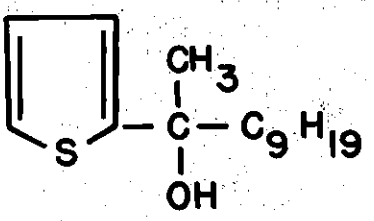
A fraction was isolated which boiled at 154°C and 14 mm. pressure.

Combustion analysis of this fraction gave results of 75.35% C and 9.89% H. The expected carbon and hydrogen content of the olefin is 75.59% C and 9.98% of H.

The refractive index and density at 20°C were 1.5172 and 0.9527, respectively. The molecular refraction as determined experimentally was 70.55. The theoretical molecular refraction for 2-(2-thienyl) decene-2 is 71.27.

The olefin was obtained in a yield of 18.32% of theoretical.

The Preparation of Methyl n-Nonyl 2-Thienylcarbinol



Eighty-five grams (0.406 moles) of n-nonyl bromide (redistilled at 169-170°C and 6 mm.) dissolved in 50 ml. of absolute ether were slowly added to 14 gm. (0.583 moles) of magnesium turnings and 50 ml. of absolute ether. The reaction apparatus was exactly similar to that described in previous experiments. A constant reflux of ether was maintained, and the reaction mixture was stirred for 30 minutes after complete addition of the bromide.

The black colored Grignard solution was cooled; 25.83 gm. (0.282 moles) of 2-acetylthiophene dissolved in 25 ml. of absolute ether were added. A yellow colored precipitate was formed in the reaction flask. White vapor was observed rising from the surface of the reaction mixture during the addition of the 2-acetylthiophene. The reaction mixture was stirred for 30 minutes after the completion of 2-acetylthiophene addition.

Hydrolysis was effected with 25% ammonium chloride; the mixture was filtered and extracted with ether. The extract was dried over anhydrous potassium carbonate. After 24 hours the K_2CO_3 was filtered out, and the ether distilled off. The residue was fractionated under reduced

pressure. Eighteen ml. of a pale yellow oil were isolated at 168°C and 6 mm. pressure.

Infrared analysis of the oil gave results which indicated the presence of the OH function.

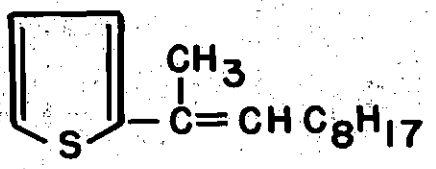
Combustion analysis of this fraction gave results of 70.08% C and 10.34% H. The theoretical carbon and hydrogen content of the olefin is 70.79% C and 10.31% H.

The molecular refraction of the product was determined to be 77.90 in comparison to the theoretical value of 77.88.

A refractive index value of 1.4940 and a density of 0.9527, both at 20°C, were observed.

The carbinol was obtained in a yield of 32.90%.

As in the case of methyl n-heptyl 2-thienylcarbinol and methyl n-octyl 2-thienylcarbinol, the initial attempt at preparing methyl n-nonyl 2-thienylcarbinol resulted in the production of the unsaturated derivative of that carbinol.



In this systhesis 14 gm. (0.583 moles) of Mg turnings were reacted with 60.5 gm. (0.292 moles) of normal nonyl bromide and 35 gm. (0.278 moles) of 2-acetylthiophene in a manner quite approximate to that employed in the preparation of 2-(2-thienyl) nonene-2 and 2-(2-thienyl) decene-2.

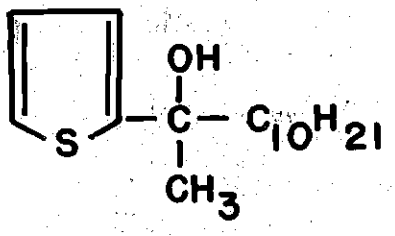
Forty-one ml. of a yellow oil boiling at 159°C and 10 mm. pressure were isolated to give a yield of 58.02%.

Combustion analysis of this product gave results of 76.54% C and 10.10% H. The theoretical carbon and hydrogen content of the olefin was calculated to be 76.19% and 10.24%, respectively.

A molecular refraction of 75.72 was observed as compared to a theoretical molecular refraction of 75.89.

The refractive index of the 2-(2-thienyl) undecene-2 at 20°C had the value of 1.5120, and the density at 20°C was found to be 0.9380.

The Preparation of Methyl n-Decyl 2-Thienylcarbinol



Methyl n-decyl 2-thienyl carbinol was prepared using the same general procedure as in the previous carbinol preparations.

Fourteen gm. (0.583 moles) of magnesium turnings and 50 ml. of absolute ether were placed in the reaction flask and 121.6 gm. (0.550 moles) of n-decyl bromide (redistilled at 113-115°C and 8-10 mm.) dissolved in 50 ml. of absolute ether were added over a period of one hour at a rate which maintained ether reflux. A Grignard solution slightly gray in color was produced. The reaction mixture was stirred for thirty minutes after the addition of all the normal decyl bromide.

The Grignard solution was cooled, and 35.6 gm. (0.282 moles) of 2-acetylthiophene dissolved in 25 ml. of absolute ether were dropped into the reaction flask over a period of 45 minutes. The formation of a yellow precipitate was observed. The reaction mixture was stirred for thirty minutes after the addition was completed.

Hydrolysis was carried out with a 25% solution of ammonium chloride. Approximately two grams of magnesium turnings were isolated upon filtering the product of hydrolysis. The filtrate was extracted with ether and dried over anhydrous potassium carbonate. The ether was evaporated and

the residue fractionated under vacuum. Thirty-six milliliters of a faint yellow oil were isolated which formed a slush upon cooling to 20°C.

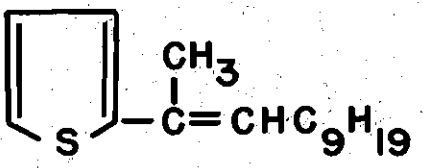
Infrared analysis of this fraction gave positive indication of the presence of the OH factor. A combustion analysis gave values of 71.21% C and 10.65% H. The theoretical carbon and hydrogen content of methyl n-decyl 2-thienylcarbinol is 71.56% C and 10.53% H.

The refractive index at 20°C was determined to be 1.4900, and the density at this temperature was 0.9424.

The molecular refraction of the carbinol was found to be 82.30 as compared to a theoretical value of 82.50.

The carbinol was obtained in a yield of 44.71%.

Two-(2-thienyl) dodecene-2 was prepared in a fashion analogous to that exercised in the preparation of the other olefin derivatives.



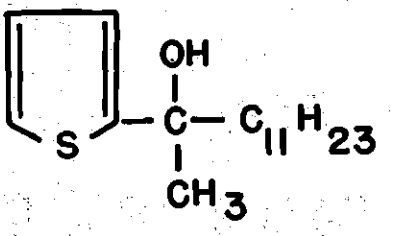
In this preparation, 127.9 gm. (0.578 moles) of normal decyl bromide dissolved in 100 ml. of absolute ether were added to 14 gm. (0.583 moles) of magnesium turnings and 50 ml. of absolute ether in the reaction flask of an apparatus setup as described previously.

Twenty milliliters of a yellow oil characterized by a singularly disagreeable odor were obtained by a vacuum distillation of the ether extract of the above described reaction mixture.

This fraction gave a combustion value of 76.23% C and 10.62% H versus the theoretical values of 76.71% C and 10.48% H for 2-(2-thienyl) dodecene-2. The observed molecular refraction was 80.00 as compared to a calculated value of 80.51.

The olefin was obtained in a yield of 13.45% of the theoretical. It boiled at 167°C and 10 mm. pressure. A refractive index value of 1.5048 and a density value of 0.9255 were observed at 20°C.

The Preparation of Methyl n-Undecyl 2-Thienylcarbinol



Eight grams of magnesium turnings (0.333 moles) and 25 ml. of absolute ether were placed into a dry three neck flask fitted with a condenser, a dropping funnel, and a mercury seal stirrer. After warming the reaction flask to the point of ether reflux, 13.79 grams (0.314 moles) of n-undecyl bromide were dropped on the magnesium.

The addition required thirty minutes and was regulated so as to maintain a constant reflux of ether. A Grignard solution which was quite black in color was produced.

Seventeen and four-tenths grams of 2-acetylthiophene (0.161 moles) dissolved in 25 ml. of absolute ether were added to the reaction flask over a period of 30 minutes. An orange colored precipitate was observed to form when the 2-acetylthiophene made contact with the Grignard solution. The reaction mixture was stirred for 30 minutes after the addition of the 2-acetylthiophene, and then hydrolyzed with 25% ammonium chloride.

The product of hydrolysis was filtered, extracted with ether, and dried over anhydrous potassium carbonate for 24 hours. The ether was distilled off at 50-60°C, and the residue was fractionated under reduced

pressure. A fourteen mililiter fraction isolated at 180°C and 14 mm. was considered to be the carbinol.

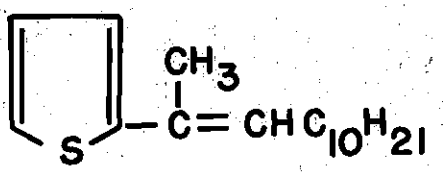
This fraction gave combustion values of 72.82% C and 10.57% H as compared to the theoretical value of 72.26% C and 10.72% H for methyl n-undecyl 2-thienylcarbinol.

Infrared analysis showed strong adsorption at 2.88 microns, indicating the presence of the OH function. A molecular refraction value of 86.45 was obtained. The theoretical molecular refraction for the carbinol is 87.12.

The pure product, a yellow pungent oil boiled at 187°C and 6 mm. pressure. The yield was 28.27% of theoretical. The product was observed to solidify at approximately 27°C.

A refractive index value of 1.4860 and a density of 0.9372 were observed. Both measurements were made at 20°C.

The olefin derivative of methyl n-undecyl 2-thienylcarbinol, 2-(2-thienyl) tridecene-2 was produced in the first attempt at the preparation of the carbinol.



In this preparation, seven grams (0.291 moles) of magnesium turnings were placed into the reaction flask with 100 ml. of absolute ether. At a regular rate, 70.3 gm. (0.299 moles) of n-undecyl bromide was dis-

solved in 100 ml. of absolute ether were added dropwise to the reaction flask. Upon complete addition of the bromide, the reaction flask was cooled for thirty minutes at 0-5°C.

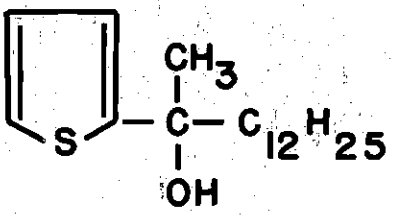
Seventy grams (0.55 moles) of 2-acetylthiophene were then dissolved in 50 ml. of absolute ether and added dropwise to the Grignard solution. The resultant reaction mixture was stirred for thirty minutes and then hydrolyzed with 15% sulfuric acid.

A small quantity of Mg turnings were filtered out of the products of hydrolysis; and ether extraction of the filtrate was effected. The extract was dried over anhydrous potassium carbonate for 24 hours, after which the ether was distilled off and the residue subjected to vacuum distillation. Eighteen grams of an oil were isolated which gave combustion values of 77.20% C and 11.40% H as compared to that expected for the olefin, 77.18% C and 10.68% H. A molecular refraction of 85.64 was obtained as compared to the theoretical value of 85.13.

The density of the 2-(2-thienyl) tridecene-2 was found to be 0.9020 at 20°C. The refractive index at the same temperature was determined to be 1.4960.

The olefin was obtained in a yield of 11.17%. It boiled at 173°C and 8 mm. pressure.

The Preparation of Methyl n-Dodecyl 2-Thienylcarbinol



Fourteen grams of magnesium turnings (0.583 moles) and 50 ml. of absolute ether were added to the reaction flask and the ether was brought to a gentle reflux. Subsequently, 136.95 grams (0.55 moles) of n-dodecyl bromide dissolved in 75 ml. of absolute ether were added to the magnesium at a constant rate over a period of 50 minutes. A black colored Grignard solution was produced. The reaction mixture was then cooled in an ice bath for thirty minutes.

Thirty-five and six-tenths grams (0.282 moles) of 2-acetylthiophene dissolved in 40 ml. of absolute ether were added to the reaction flask over 30 minutes. The complex formed was stirred for an additional 30 minutes.

After hydrolysis, extraction, and drying, the extract was distilled to remove most of the ether, and the residue was subjected to vacuum distillation. A fraction was isolated at 210°C and 14 mm. pressure which was observed to solidify at 37°C.

By dissolving the product in ether and then adding an excess of ethyl alcohol, a small quantity of a white, waxy material was obtained which gave a melting point value of 48-49°C. Not enough material was

collected to suffice for combustion analysis.

By distilling off the ether and the alcohol utilized in the isolation of the waxy material, a light yellow oil was again isolated which was observed to form a semisolid at 24°C. Combustion analysis of this material gave the results 72.38% C and 11.06% H as compared to the theoretical values of 72.38% C and 10.89% H for the carbinol. The molecular refraction was determined to be 89.50. The theoretical molecular refraction for methyl n-dodecyl 2-thienylcarbinol is 9174.

The density of the oil was found to be 0.9379 at 20°C, and the refractive index was determined to be 1.4810 at the same temperature.

CHAPTER IV

SUMMARY AND DISCUSSION

CHAPTER IV

SUMMARY AND DISCUSSION

The original purpose of this investigation was the preparation of the dialkyl thienylcarbinols, methyl n-heptyl 2-thienylcarbinol, methyl n-octyl 2-thienylcarbinol, methyl n-nonyl 2-thienylcarbinol, methyl n-decyl 2-thienylcarbinol, methyl n-undecyl 2-thienylcarbinol, and methyl n-dodecyl 2-thienylcarbinol. Initial attempts at the syntheses of all but the last of these carbinols, however, led to the production of materials which gave combustion analyses and molecular refraction values very approximate to those expected of the dehydration products of the carbinols. This assumption was substantially confirmed later in the isolation of the alcohols.

With the isolation and the determination of the various properties of the olefins there yet remained the task of preparing the alcohols. Since these olefins were most likely produced as a result of carbinol dehydration, it was decided that a less strenuous plan of reaction would facilitate the development of the alcohols. After several reaction attempts, the carbinols became attainable. Reaction modifications were effected in several ways.

1. Less 2-acetylthiophene (0.282 moles rather than 0.55 moles) was used for each 0.583 moles of magnesium reacted.
2. Ten percent H_2SO_4 was replaced by 25% NH_4Cl in ice as the hydrolyzing agent.

3. The temperature of vacuum distillation was lowered about 10-15°C by substituting a boiling stick for the ebullition tube initially used.
4. Vacuum distillation was carried out at a more rapid rate. Yields in the case of the carbinols varied from 28.87% to 54.29% and the yield of the olefins from 11.17%-58.02%.

In ascending both the series $C_nH_{2n-4}SO$ and the series $C_nH_{2n-6}S$, the refractive index values were observed to decrease. The rates of decrease when plotted against the introduced side chain, gave relationships which approached the linear. The refractive index values of the olefins were from 0.0100 to 0.0187 above the values for the carbinols. All of the refractive index values were determined with an Abbe refractometer, the prisms of which were maintained at a constant temperature of 20°C by water from a constant temperature bath.

All the density measurements were made at 20°C with a bottle type pycknometer. The rate of decrease of density with side chain gave a fairly smooth relationship for both the carbinols and the olefins. The carbinol densities exceeded the corresponding olefin densities from 0.0142 to 0.0352 with the difference in values becoming more prominent ascending the series. A plot of density versus side chain for the carbinols gave rise to smooth curve relationship which seems to be approaching a maximum at about 0.9300. A converse relationship was observed between the olefins and their densities. The density values gave strong indication of decreasing more rapidly as the complexity of the side

chain introduced was increased.

The combustion determinations were made on an apparatus arrangement quite similar to that described by Fischer[4]. The apparatus was but slightly modified. Two furnace units rather than three were used to heat the combustion tube, and a ceric nitrate plug was not inserted into the combustion tube as suggested by Fischer. Erratic combustion results were not too infrequently obtained, and it was necessary, as a rule, to make runs until several corresponding results were obtained. The accuracy of the apparatus seemed to be severely disturbed by high humidity.

Molecular refractions were determined by use of the Lorentz-Lorentz equation. The values for the atomic refractions of carton and hydrogen were taken from standard tables[5]. The values for the atomic refraction of sulfur was that determined by Price and Twiss[6].

The carbinols were faintly yellow colored oils rather pungent in odor. The olefins were yellow oils having a disagreeable odor. The yellow color of the carbinols was observed to become more intense with long exposure to heat and light. Apparently heat and light over a period of time were sufficient to cause alcohol dehydration.

All of the normal bromides used in the previously described experiments, with the exception of normal decyl bromide, were secured from the Columbia Organic Chemicals Company. The normal decyl bromide was

---

[4]Fischer Laboratory Manual of Organic Chemistry

[5]Landolt-Bornstein, Physakilisch-Chemische Tabellen vol. 5, p. 985

[6]Price, T.S., and Twiss, D.F., J. Chem. Soc., 101, 1263 (1912)

purchased from the Matheson Company, Inc.

The magnesium turnings were a part of lot no. 31848 from the J. T. Baker Company of Phillipsburg, New Jersey.

The absolute ether utilized was of two lots. That used in the preparation of the olefins was prepared by washing commercial ether with a saturated ammonium chloride solution, storing over anhydrous $CaCl_2$ for a week, and then after rapid filtration, drying over sodium wire. The absolute ether utilized in the preparation of the carbinols was secured from Merck and Company of Rahway, New Jersey, and was a part of lot 71633.

BIBLIOGRAPHY

BIBLIOGRAPHY

Beaver, William M., "Tertiary Alcohol Derivatives of 2-Acetylthiophene," Thesis, School of Chemistry, Georgia Institute of Technology, 1950

Fieser, L. F., and Fieser, M., Organic Chemistry, 1944., D. Heath and Co., p. 129

Fischer, H. L., Laboratory Manual of Organic Chemistry, John Wiley and Sons, New York

Landbolt-Bornstein, Physikalischen Chemische Tabellen, Vol. 5, p. 985

Price, T. S., and Twiss, D. F., J. Chem. Soc.101, 1263 (1912)

Thomas V., Compte rendus 146, 643

APPENDIX I

TABLE I-A

PHYSICAL PROPERTIES

Carbinol	Yield %	B.P. °C	Press. mm.	Density 20°	Ref.Index 20°
Methyl n-heptyl 2-thienyl	54.29	146-7	12	0.9897	1.5035
Methyl n-octyl 2-thienyl	37.06	161	14	0.9669	1.5023
Methyl n-nonyl 2-thienyl	32.90	172	12	0.9527	1.4940
Methyl n-decyl 2-thienyl	44.71	182	12	0.9424	1.4900
Methyl n-undecyl 2-thienyl	28.87	187	6	0.9379	1.4860
Methyl n-dodecyl 2-thienyl	33.67	198	12	0.9372	1.4810

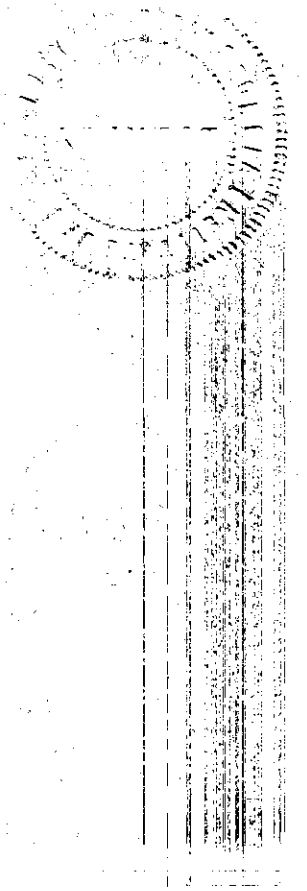


TABLE I-B

PHYSICAL PROPERTIES

Olefin	Yield %	B.P. °C	Press. mm.	Density 20°	Ref. Index 20°
2-(2-thienyl) nonene-2	33.61	142	10	0.9623	1.5222
2-(2-thienyl) decene-2	18.32	154	14	0.9527	1.5172
2-(2-thienyl) undecene-2	58.02	159	10	0.9380	1.5120
2-(2-thienyl) dodecene-2	13.45	167	10	0.9255	1.5048
2-(2-thienyl) tridecene-2	11.17	173	8	0.9020	1.4960

TABLE II-A

ANALYSIS

Carbinol	Molecular Ref. Found	Molecular Ref. Cal.	Carbon Found	Carbon Cal.	Hydrogen Found	Hydrogen Cal.
Methyl n-heptyl 2-thienyl	67.64	68.64	68.44	68.96	9.79	9.80
Methyl n-octyl 2-thienyl	72.00	73.26	70.63	69.92	10.16	10.07
Methyl n-nonyl 2-thienyl	77.90	77.88	70.08	70.79	10.34	10.31
Methyl n-decyl 2-thienyl	82.30	82.50	71.21	71.56	10.65	10.53
Methyl n-undecyl 2-thienyl	86.45	87.12	72.82	72.26	10.57	10.72
Methyl n-dodecyl 2-thienyl	89.50	91.74	72.38	72.89	11.06	10.89

TABLE II-B

ANALYSIS

Olefin	Molecular Ref. Found	Molecular Ref. Cal.	Carbon Found	Carbon Cal.	Hydrogen Found	Hydrogen Cal.
2-(2-thienyl) nonene-2	65.68	66.65	74.66	74.81	9.76	9.69
2-(2-thienyl) decene-2	70.55	71.27	75.35	75.59	9.89	9.98
2-(2-thienyl) undecene-2	75.72	75.89	76.54	76.19	10.10	10.24
2-(2-thienyl) dodecene-2	80.00	80.51	76.23	76.71	10.62	10.48
2-(2-thienyl) tridecene-2	85.64	85.13	77.20	77.18	11.40	10.68

APPENDIX II

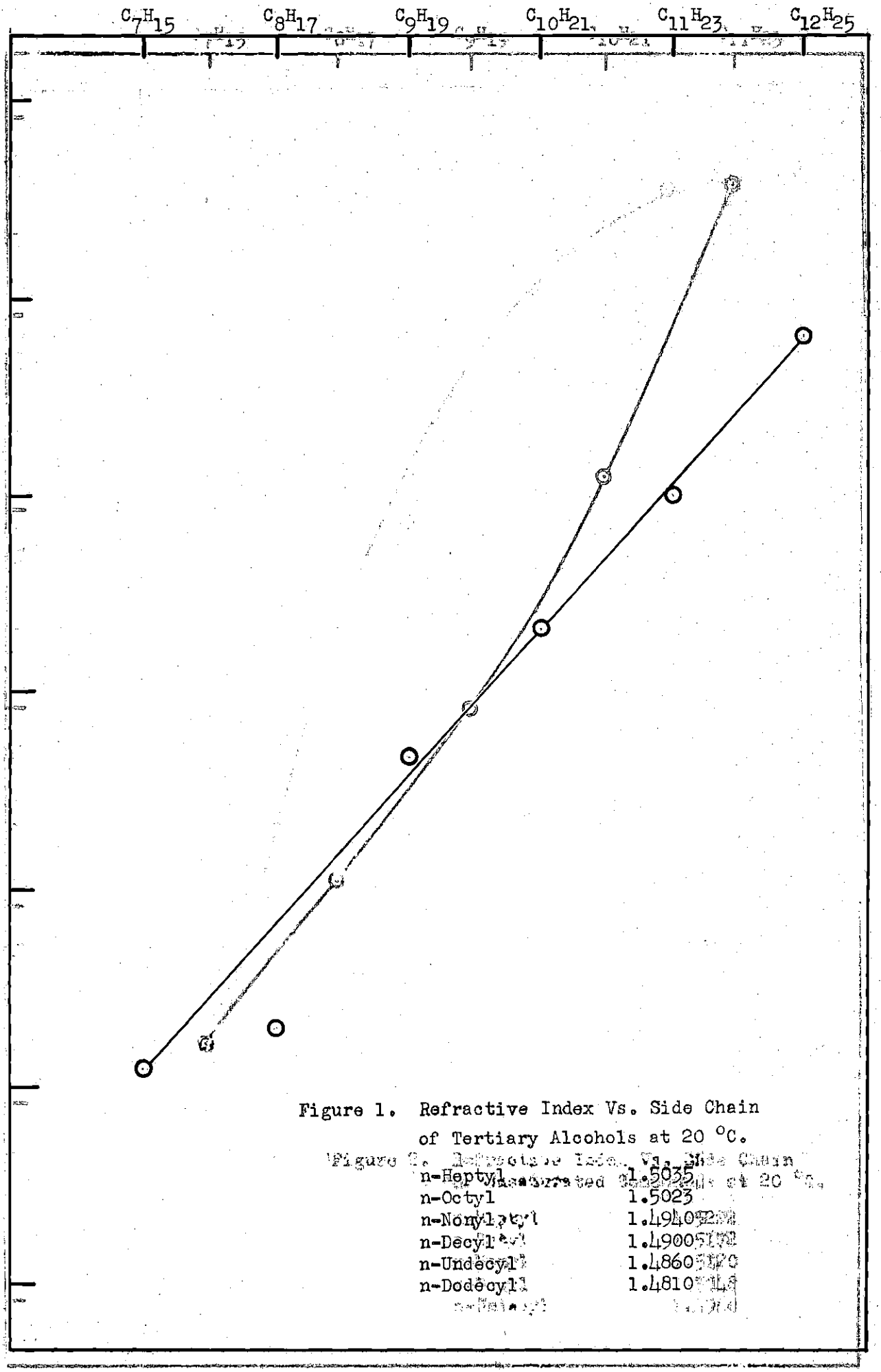


Figure 1. Refractive Index Vs. Side Chain of Tertiary Alcohols at 20 °C.

n-Heptyl	1.5035
n-Octyl	1.5023
n-Nonyl	1.4940
n-Decyl	1.4900
n-Undecyl	1.4860
n-Dodecyl	1.4810

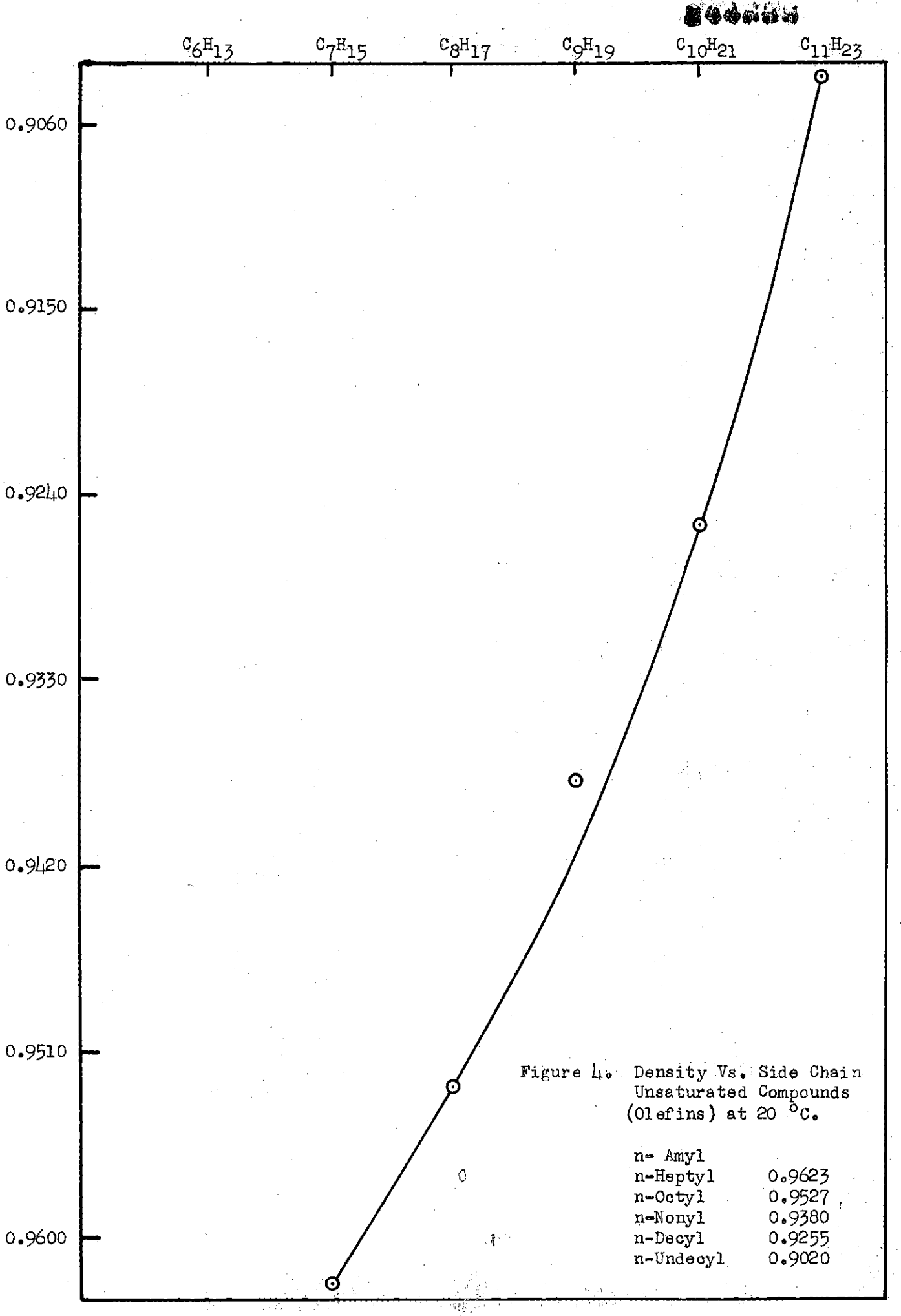


Figure 4. Density Vs. Side Chain Unsaturated Compounds (Olefins) at 20 °C.

n- Amyl	
n-Heptyl	0.9623
n-Octyl	0.9527
n-Nonyl	0.9380
n-Decyl	0.9255
n-Undecyl	0.9020